DETAILED MECHANISTIC
OF THE SYNTHESIS OF OXYGENATES FROM CO/H$_2$

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INTRODUCTION

The traditional interest for the synthesis of higher oxygenates from CO and H$_2$ mixtures has been recently focused on the accomplishment of high selectivities towards α-branched alcohols, such as 2-methyl-propanol and 2-methyl-butanol, which can be exploited as precursors for the synthesis of ethers (MTBE, TAME) with high octane properties [1]. Indeed isobutanol is the most abundant product of Higher Alcohol Synthesis (HAS); however, more than 100 other compounds are formed by hydrogenation of CO [2], among which commercially undesired oxygenates are also included. HAS product distribution is strongly affected by the operating conditions under which the reaction is carried out: contact time, temperature, feed composition control, infact, the yield and selectivity of the different classes of species produced. The development of an industrial process for the synthesis of branched alcohols calls for a rational optimization of the operating conditions, which may be accomplished only by means of a reliable kinetic treatment of the reacting system. Detailed kinetic models of HAS have been proposed for both the low-temperature [3] and the high-temperature [4] modified methanol catalysts; however, so far no kinetic analysis has been published which can predict the whole distribution of HAS products as a function of all the operating variables.

In the following we present the development of a mechanistic kinetic model of HAS over Cs-promoted Zn/Cr/O catalysts aimed to design purposes; the model translates the bulk of indipendent observations concerning the mechanism and the thermodynamic constraints involved in the chain-groth process.

HAS REACTION NETWORK

An extensive study was performed in the past on the evolution and reactivity of the surface intermediates involved in HAS, consisting in steady-state microreactor experiments, Temperature Programmed Desorption (TPD) and Surface Reaction (TPSR) of a wide variety of oxigenated C$_1$-C$_5$ probe molecules [5, 6]; three major chemical routes were thus identified as responsible of the chain growth process:

1) the *aldol-type condensation* beween carbonylic species, giving rise to the formation of branched higher aldehydes or ketones according to a "normal" or "oxygen-retention reversal" (ORR) evolution of the surface intermediate [7];

2) the so-called *α-addition* of a C$_1$ nucleophilic specie to higher aldehydes;

3) the *ketonization reaction*, responsible of the formation of ketones *via* decarboxylative condensation of two aldehydes.

Toghether with a first C$_1$->C$_2$ step, such reactions can explain the whole variety of observed under synthesis conditions.

While the chain growth proceeds in a kinetic regime, other reactions also involved in HAS have been proved to be governed by chemical equilibrium. They include: the methanol synthesis, the hydrogenation of aldehydes and ketones to primary and secondary alcohols respectively, the ketonization reactions, the water gas shift reaction and the synthesis of methyl-esters [8].

DEVELOPMENT OF A MECHANISTIC KINETIC MODEL OF HAS

The reaction network above presented has been validated on a quantitative basis by the formulation of a kinetic analysis [4] able to reproduce HAS product distribution for specified values of the operating conditions. Such original treatment has been recently modified and adapted to optimization purposes, that is to obtain a comphehensive and predictive desciption of the reacting system as function of the major operating variables. The development of the final

kinetic model can schematized as follows in three subsequent steps:

1) *Identification of the reacting species*. Based on the experimental evidences, classes of reactants have been defined for each reaction included in the kinetic scheme. Namely, for the case of aldol condensations a nucleophilic behavior has been attributed to all the carbonylic species with no α-branching, while an electophilic behavior has been attributed to the C_1-C_6 aldehydes, both linear and branched. The nature of formaldehyde has been assumed for the C_1 intermediate involved in α-additions, which have been considered to interest the whole class of aldehydes as possible electrophilic reactants. Finally, for each ketone a contribute of formation via ketonization has been included.

2) *Chemical lumping*. Reaction rates and specie reactivities have been diversified along the line of the experimental observations. In the case of aldol condensations an intrinsic kinetic constant (function of reaction temperature, only) has been defined, but a set of further relative rate constants has been introduced in order to characterize the possible chain growth pathway (Normal or ORR), the nature of the nucleophilic reactant (aldehyde or ketone), the structure of the electrophilic agent (linear or branched). Similar diversification has been applied to the cases of α-additions and ketonizations.

3) *Formulation of model equations*. Mass balances have been written for all the reacting species; the rate expressions were based on a Langmuir-Hinshelwood mechanism taking into account the competitive adsorption of water on the catalyst active sites. Assumed an isothermal PRF model for the synthesis reactor, the model resulted in 42 differential mass balances for carbonyl species, 42 algebraic equations accounting for the hydrogenation equilibria between carbonyl species and corresponding alcohols, the balances for CO, H_2, H_2O, CO_2.

RESULTS

The model parameters were estimated from multiresponse non linear regression on 11 kinetic runs performed over a Cs-doped Zn/Cr/O catalysts. The comparison between experimental and calculated effects of H_2/CO feed ratio, CO_2 feed content and reaction pressure are reported in Fig. 1-3 (symbols = experimental data, lines = model calculations).

* *Effect of H$_2$/CO feed ratio*. As shown in Fig. 1a methanol concentration is maximum when a stoichiometric mixture of H_2 and CO is fed. The model reproduces correctly the experimental data, due to the assumption of chemical equilibrium for methanol synthesis. Higher alcohol concentrations present smooth maximum-wise trends with growing values of H_2/CO feed ratio in the range 0.5-1.5; the model predicts with accuracy that the highest productivities can be obtained for H_2/CO values close to 1. and 0.5, in the cases of primary alcohols (Fig. 1a-b) and ketones (Fig. 1c) respectively. Both experimental data and model calculations indicate that at high values of hydrogen partial pressures, a significant drop in the formation of the C_{2+} oxygenates occur.

* *Effect of CO2 feed content*. The presence of CO_2 in the feed stream causes an overall decreasing of higher alcohols production (Fig. 2a-c). Such effect is however mostly emphasized in the case of the oxygenates with terminal behavior (isobutanol), while modest in the case of the intermediates species (ethanol): thus, the product distribution changes, with increasing fraction of CO_2, in the direction of a growing molar ratio between low and high molecular weight components. These features are well reproduced by the kinetic treatment that can explain the inhibiting effect of CO_2 on HAS by accounting for the competitive adsorption of water on the catalyst active sites; notably, water concentration increases significantly with growing CO_2 partial pressure due the thermodynamic equilibrium which governs the water gas shift reaction.

* *Effect of reaction pressure*. A slight promotion of HAS is obtained by increasing the reaction pressure in the range 85-100 atm (Fig. 3a-c). Experimental and calculated results show, however, that such promotion is accompanied by a significant loss in the relative selectivity higher alcohol/methanol; methanol formation is, infact, strongly enhanced at high pressures. The model fitting apprears satisfactory. We note that the adoption of a first order depence with respect to CO partial pressure for the kinetics of the C_1->C_2 reaction has been decisive for a proper simulation of the pressure effect; this results on the contrary overestimated when the formation of the first C-C bond is described by second order kinetics, in analogy with the chain-growth reactions (e. g. aldol condensations).

The match between experimental data and model previsions is extremely satisfactory and suggests an overall adequacy of the kinetic model (reaction mechanism, kinetic expressions, diversification of the reactivities). However, we have verified to a more stringent level the chemical costistency of our treatment by adopting of a perturbative approach: we have infact applied the model to the simulation of chemical enrichment experiments. The comparison between calculated and experimental effect of adding an oxigenate (ethanol, propanol, 2-butanone) to the feed stream turned out to be highly informative on the accuracy with which reaction mechanism and the relative reactivities of the intermediates are decribed.

* *Addition of ethanol.* In this case a global promotion of HAS is underlined experimentally observed. If compared to reference conditions where only syngas if fed to the reactor, the products mixture obtained with an ethanol-containing feed stream presents higher amounts of linear and branched primary alcohols, as well as of ketones (Fig. 4-a). This is in line with the well known high reactivity of the C_2 intermediate. Simulating the addition of ethanol, also the calculated product mixture distribution changes towards an increased amount of all the major classes of products (Fig. 4-b); such result proves that the model is able to reproduce correctly the key role of the intermediate specie and the network of chemical patterns which spread from it involving the whole reacting system. It is on the other hand evident that the model tends to overestimate the promotion of ketones formation, which has been related to an overestimation of the role of ketonization reactions in the kinetic scheme. We note, however, that ketones are only secondary products of HAS, their outlet concentration being usually one order of magnitude lower than the concentration of primary alcohols.

CONCLUSIONS

A mechanistic kinetic model of HAS over Cs-promoted Zn/Cr/O catalysts has been developed, the final aim being its application to process design purposes. The model adequacy has been tested by comparison with a set of kinetic data obtained under typical synthesis conditions and with the results of chemical enrichment experiments; the former are specifically demanding for a quantitative adequacy of the kinetic scheme, the latter are instead more informative on the accuracy with which the details of the reaction mechanism are taken into account. A satisfactory description of the reacting system has been obtained over a wide operational field; in line with the experimental results, the model calculations suggest that an equimolar H_2/CO feed ratio and absence of CO_2 in the feed stream are optimal conditions for the synthesis of branched oxygenates. Increments of the total pressure are then estimated to lead to a lowering of the relative higher alcohol/methanol selectivity.

ACKNOWLEDGEMENT

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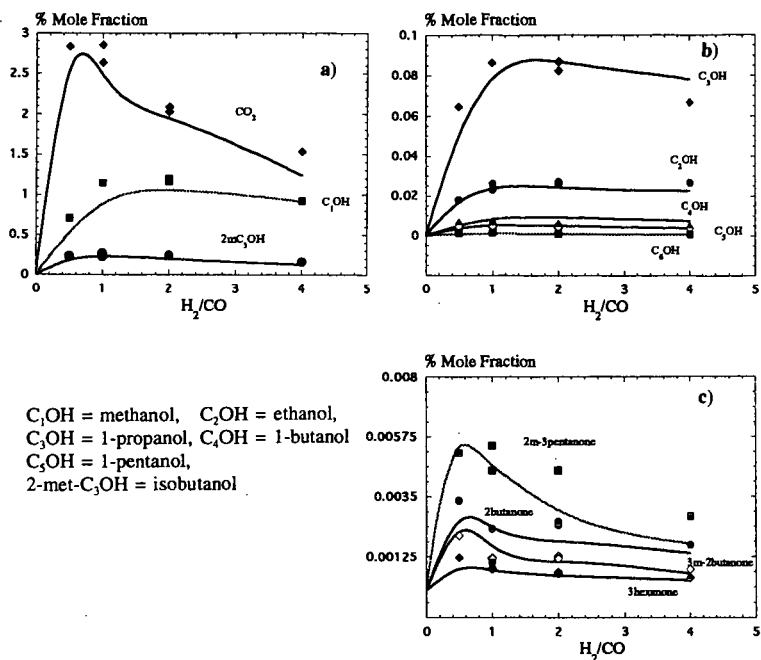
C₁OH = methanol, C₂OH = ethanol,
C₃OH = 1-propanol, C₄OH = 1-butanol
C₅OH = 1-pentanol,
2-met-C₃OH = isobutanol

Fig 1. Calculated (lines) and experimental (symbols) effect of H_2/CO feed ratio on HAS product distribution. T = 405°C, P = 85 atm, CO_2 = 0 %, GHSV = 8000 h^{-1}.

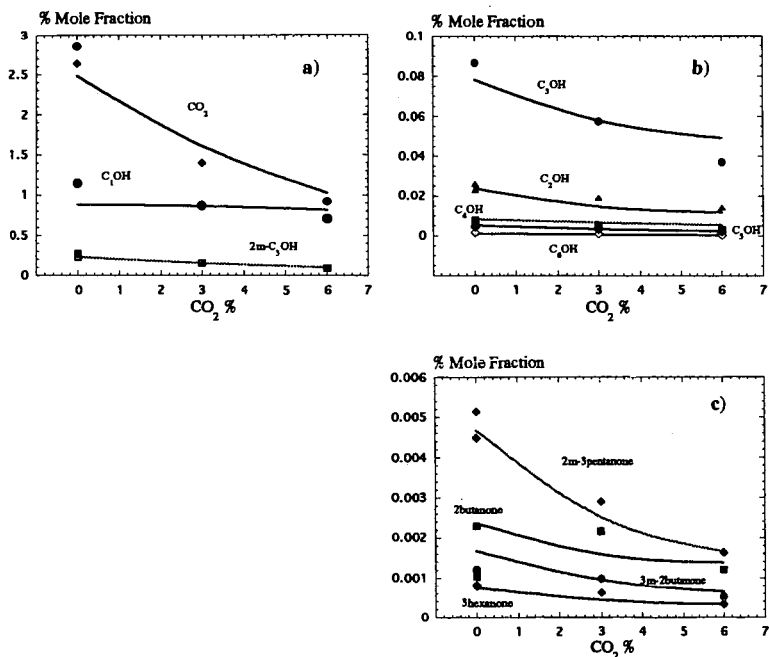**Fig. 2.** Experimental and calculated effect of CO_2 feed content. T = 405°C, P = 85 atm, H_2/CO = 1, GHSV = 8000 h^{-1}.
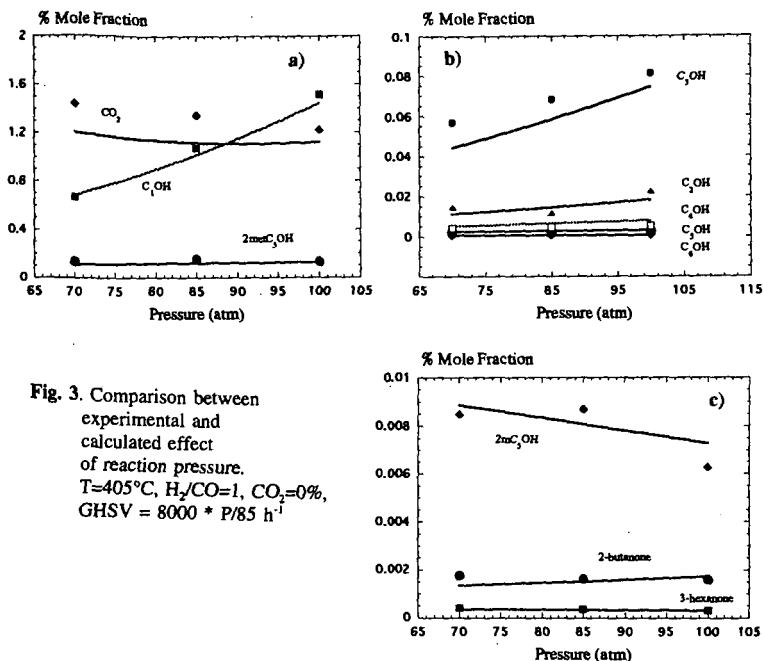
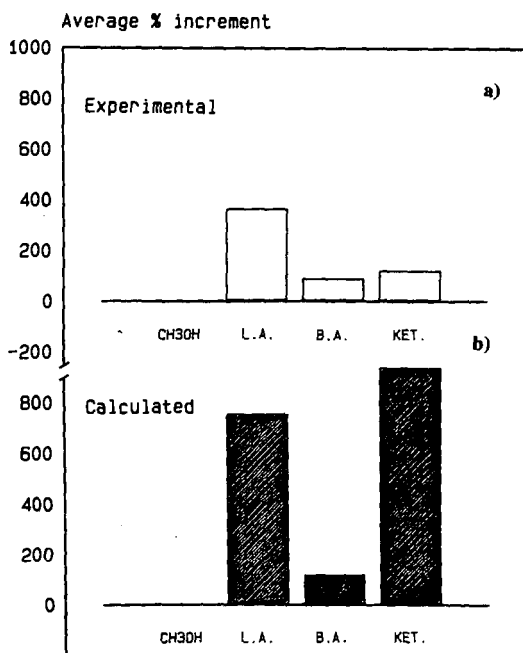**Fig. 3.** Comparison between experimental and calculated effect of reaction pressure. T=405°C, $H_2/CO=1$, $CO_2=0\%$, GHSV = 8000 * P/85 h^{-1}

Fig. 4. Experimental versus calculated effect of ethanol addition on grouped HAS product distribution. T = 405°C, P = 85 atm, H_2/CO = 1, ethanol = 2 %, CO_2 = 0 %, GHSV = 8000 h^{-1}. The effect is expressed as average percentage increment of the molar fraction with respect to absence of ethanol in the feed stream for L.A.=linear alcohols (ethanol excluded), B.A.=branched alcohols, KET.=ketones.